Direct Observation of Surface Ethyl to Ethane Interconversion upon C_2H_4 Hydrogenation over Pt/Al_2O_3 Catalyst by Time-Resolved FT-IR Spectroscopy
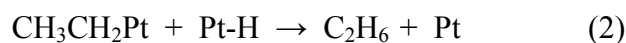
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Abstract

Time-resolved FT-IR spectra of ethylene hydrogenation over alumina-supported Pt catalyst were recorded at 25 ms resolution in the temperature range 323 to 473 K using various H_2 flow rates (1 atm total gas pressure). Surface ethyl species (2870 and 1200 cm^{-1}) were detected at all temperatures along with the gas phase ethane product (2954 and 2893 cm^{-1}). The CH_3CH_2Pt growth was instantaneous on the time scale of 25 ms under all experimental conditions. At 323 K, the decay time of surface ethyl (122 $\pm$ 10 ms) coincides with the rise time of C_2H_6 (144 $\pm$ 14 ms). This establishes direct kinetic evidence for surface ethyl as the kinetically relevant intermediate. Such a direct link between the temporal behavior of an observed intermediate and the final product growth in a heterogeneous catalytic system has not been demonstrated before to our knowledge. A fraction (10 percent) of the asymptotic ethane growth at 323 K is prompt, indicating that there are surface ethyl species that react much faster than the majority of the CH_3CH_2Pt intermediates. The dispersive kinetics is attributed to the varying strength of interaction of the ethyl species with the Pt surface caused by heterogeneity of the surface environment. At 473 K, the majority of ethyl intermediates are hydrogenated prior to the recording of the first time slice (24 ms), and a correspondingly large prompt growth of ethane is observed. The yield and kinetics of the surface ethylidyne are in agreement with the known spectator nature of this species.

1. Introduction

Efforts to understand the detailed mechanism of heterogeneous catalytic hydrogenation of ethylene over noble metal catalysts continues to be of intense interest despite the large number of studies on this subject by many groups.[1] Hydrogenation of alkenes is of major industrial importance,[2] and the prototype C_2H_4 system has long served as a main focus for advancing the knowledge of this reaction type. In particular, vibrational spectroscopic studies of the reaction over single crystal Pt surfaces or finely dispersed Pt particles on silica or alumina under steady-state conditions[1] led to the acceptance of stepwise hydrogenation mechanism originally proposed by Horiuti and Polanyi.[3] In this mechanism, surface adsorbed ethylene is hydrogenated to ethyl and subsequently converted to ethane.

$$C_2H_4 \; + \; Pt\text{-}H \;\; \rightarrow \;\; CH_3CH_2Pt \qquad (1)$$

$$CH_3CH_2Pt \; + \; Pt\text{-}H \; \rightarrow \; C_2H_6 \; + \; Pt \qquad (2)$$

Adsorbed ethylene is known to exist in a weakly π-bonded or more strongly di-σ-bonded form based on reflection-absorption infrared and HREELS studies on Pt(111) surfaces,[4-8] and transmission IR spectroscopy of supported metal particle catalysts.[9,10] Various experimental studies have provided convincing evidence that the hydrogenation step (1) involves π-C_2H_4 species.[11-16] Using sum frequency generation spectroscopy (SFG) for monitoring the CH stretching region, Somorjai and coworkers have identified absorption bands of π-bonded ethylene over Pt(111) under high pressure conditions at room temperature and demonstrated that it is the species being hydrogenated.[1b,15] The same

study revealed peaks assigned to surface ethyl species, hydrogenation of which was proposed to constitute the main reaction path.

π-C_2H_4 and ethyl species were also detected by FT-IR in steady state hydrogenation experiments over supported IR clusters.[17] On the other hand, the ethylidyne surface species (CH_3CPt_3) familiar from early HREELS and reflection-absorption infrared surface work [8,9,18,19] was determined to play no kinetically significant role in the catalytic hydrogenation.[9,20,21] These experimental findings on Pt or Pd surfaces are supported by recent DFT computational work.[22-25] The papers predict that the barrier to hydrogenation is substantially lower for π-C_2H_4 than for di-σ ethylene (at the high surface coverage relevant for reaction conditions), and that the barrier for ethyl to ethane conversion exceeds that of step (1) by a factor between 2 and 5.

In an attempt to obtain direct evidence for the kinetic relevancy of the ethyl intermediate of C_2H_4 hydrogenation under reaction conditions, we have monitored the catalysis by time-resolved FT-IR spectroscopy using the rapid-scan method. A preliminary study of the catalysis over alumina-supported Pt catalyst at 473 K under continuous H_2/N_2 flow (1 atm) and pulsed release of C_2H_4 (30 ms duration) revealed two transient intermediates, namely ethylidyne (2880 and 1339 cm^{-1}) and a species absorbing at 1200 cm^{-1}, assigned to surface ethyl.[26] The rise of both intermediates was too fast to be resolved on the 100 ms time scale. As expected, the decay time of the CH_3CH_2Pt species (around the time limit of 100 ms) was faster than that of CH_3CPt_3 (300 ms). Nevertheless, given the vast difference in their mechanistic role (ethylidyne is a mere spectator)[1b], the lifetimes of the two surface species were surprisingly close. Moreover, the ethane growth was already

close to its maximum in the first recorded time slice, suggesting that the ethyl species exhibits dispersive hydrogenation kinetics with the majority of the intermediates reacting at times shorter than 100 ms when running at 473 K.

In order to establish the kinetic relationship between the decay of the surface ethyl species and the rise of the gas phase ethane, we have conducted a comprehensive FT-IR study of the temperature (323-473 K) and hydrogen concentration dependence of the temporal behavior of the $C_2H_4 + H_2$ reaction over Pt/Al_2O_3 at 25 ms resolution. Taking advantage of the slower kinetics at the lower temperatures, we show in this paper that the surface ethyl decay coincides with the rate of ethane growth, thus demonstrating directly the kinetic relevancy of the surface ethyl intermediate.

2. Experimental Section

Time-resolved FT-IR spectra were recorded in the rapid-scan mode on a Bruker model IFS88 spectrometer equipped with a HgCdTe PV detector Kolmar Technologies model KMPV8-1-J2 (8 micron bandgap) or a HgCdTe PV detector model KMPV11-1-J2 (12 micron bandgap). The mirror velocity was 160 kHz, and the spectral resolution was 4 cm^{-1}. The protocol for obtaining the transient spectra consisted of the recording of 99 interferograms (double-sided/ forward-backward) following a C_2H_4 pulse, corresponding to 396 single-sided interferograms. Four spectral time slices of 25 ms duration were extracted from the first and four more from the second forward-backward mirror motion

after the ethylene pulse, while the 4 interferograms of each subsequent forward-backward motion were automatically averaged for S/N improvement, furnishing spectral time slices at 128 ms resolution. A total of 50 such sets of single beam spectra generated by 50 ethylene pulses were stored as the result of one experiment. Final time-resolved spectra for a given time delay were obtained by calculating the ratio of each of the 50 corresponding stored single beam spectra against the single beam spectrum taken just before the pulse. The 50 ratioed spectra were then averaged to yield the absorbance time slice for a given time delay. The results of 10 such experiments were averaged for further S/N improvement.

The Al_2O_3-supported, finely divided Pt catalyst (Exxon HFR-100, 5% Pt, calcined at 823 K, BET surface area 180 m^2g^{-1}) was prepared in the form of a pressed wafer with an embedded W grid. The catalyst material was provided by Dr. Joel Ager at LBNL. The latter is made of a 0.49 in. diameter tungsten foil (thickness 0.002 in.) featuring laser-drilled 0.012 in. holes. The grid, which was held by a Ni jaw similar to a design described by Yates[27] was electrically heated and the temperature monitored by a thermocouple mounted on the W grid. The catalyst was situated in the center of home built 100 cm^3 stainless steel reactor cell equipped with two flange-mounted BaF_2 windows for transmission infrared spectroscopy. The catalyst was transparent in the region 5000-800 cm^{-1} (reduced sensitivity below 1100 cm^{-1} because of Al-O stretch absorption). The continuous flow of a H_2/N_2 mixture (4.5 L min^{-1}, ratio 0.053 unless noted otherwise, total pressure 1 atm) entered the cell through a ¼ in. tube on one side and exited through an exhaust line on the other. The flow of each gas was regulated by MFC valves (MKS

Instruments). Millisecond time resolution was achieved by the synchronization of ethylene

pulses of 30 ms duration with the forward motion of the interferometer mirror.[28] The

spacing between ethylene pulses was 12.8 s, which assured that all reaction had ceased

prior to arrival of a fresh pulse. The pulses were released through a fast value (General

Valve Series 99 pulsed valve coupled with an Iota One pulse driver) and contained 3

micromol C_2H_4 (85 psi back pressure). The pulses merged with the continuous H_2/N_2 flow

7 cm upstream from the center of the reactor cell. Before each series of experiments, the

Pt/Al_2O_3 catalyst was exposed for at least 2 h to a H_2/N_2 flow at 473 K in order to assure

complete reduction of the Pt surface. Ethylene (Matheson, 99.999%), hydrogen (Air Gas,

99.9999%), and nitrogen (Air Gas, 99.9995%) gas were used as received.

3. Results

3.1 Reaction at 323 K

Survey spectra of four time slices at 25 ms resolution are shown in Figure 1. The bottom

trace is the first spectrum recorded after the C_2H_4 pulse, with its midpoint delayed by 24 ms

relative to the opening of the pulsed ethylene valve. Subsequent traces shown are at 107,

235, and 6,000 ms. The most prominent bands are the gas phase absorptions of C_2H_4 at

3000 cm^{-1} (v_9 and v_{11}), 1890 cm^{-1} ($v_7 + v_8$), 1440 cm^{-1} (v_{12}), and 950 cm^{-1} (v_7).[29] The

ethylene gas phase bands are the strongest in the first time slice and then decrease,

principally due to removal of the reactant from the infrared viewing zone by gas flow.[26]

The kinetics of the ethylene decrease is displayed in Figure 2. The depletion observed at

2050 cm^{-1} is attributed to loss of Pt-H absorption.[26] The presence of CO, which also

absorbs around 2050 cm^{-1}, was ruled out by experiments with D_2.[26]

More interestingly, the survey spectra reveal additional bands at 2893, 2870, 1339, and

1200 cm^{-1} whose kinetic behavior is very different from that of ethylene. These

absorptions were already observed in the 100 ms spectra recorded previously at 473 K

and attributed to gas phase ethane (2893 cm^{-1}, $\nu_8+\nu_{11}$)[26,30], surface ethylidyne (CH_3CPt_3,

2880 and 1339 cm^{-1}), and surface ethyl species (CH_3CH_2Pt, 2870 and 1200 cm^{-1}).[26]

However, the improved sensitivity, time resolution and lower reaction temperatures

reported here furnish crucial kinetic insights not accessible in our preliminary study. The

ethane band at 2893 cm^{-1} grows during the initial 200 ms period and then starts to

decrease. Computer subtraction of C_2H_4 absorption facilitates the kinetic analysis of the

ethane band. Precise spectral subtraction is achieved by adjusting the intensity of the

C_2H_4 spectrum so that the 1890 cm^{-1} band cancels completely (the region is free of

overlap with any other species). The spectra are shown in Figure 3a, and the absorbance

growth kinetics including a single exponential fit, in Figure 3b. Determination of the

latter required that each spectral trace was corrected for the loss of product by removal

through gas flow, which is evident from the observed decrease of the 2893 cm^{-1} peak at

times greater than 200 ms. Since the ethane molecules join the flow of the C_2H_4-N_2-H_2

gas mixture upon desorption from the Pt surface, the rate of removal of C_2H_6 from the

viewing zone is the same as that of ethylene. Therefore, the C_2H_6 band at time t was

normalized by the factor $[C_2H_4]_{24msec}/[C_2H_4]_t$ taken from Figure 2. Comparison with an

authentic spectrum of gaseous C_2H_6 recorded with identical spectral parameters (bottom

trace of Figure 3a) shows that the spectral subtraction reveals the ν_5(CH) mode of ethane at 2954 cm^{-1} in addition to the 2893 cm^{-1} band already observed in the raw spectra.[30] The growth of the two ethane bands is identical within uncertainties, with a 1/e rise time of 144 ± 14 ms. The C_2H_6 product also absorbs at 2880 cm^{-1} (P branch of $\nu_8+\nu_{11}$), but this band is overlapped by surface ethyl absorption in the initial time slices. Ethylidyne is also known to absorb at 2880 cm^{-1}.[10] However, the growth of CH_3CPt_3 is too small at 323 K even on the hundreds of ms time scale for detecting its CH stretch absorption (see below). The surface ethyl species contribution to the spectrum in the ν(CH) region can be seen when comparing the first time slices of Figure 3a (t = 24 and 107 ms), shown in Figure 4 on an expanded scale for clarity; the 2880 cm^{-1} peak and the shoulder at 2870 cm^{-1} in the 24 ms spectrum are too strong for sole attribution to ethane, with its gas phase peak at 2893 cm^{-1}. By contrast, at 107 ms the 2880 and 2870 cm^{-1} absorptions of CH_3CH_2Pt are overwhelmed completely by the C_2H_6 spectrum.

Figure 5 shows the decay kinetics of the transient 1200 cm^{-1} band assigned to surface ethyl species.[26] We find that the decay time of 122 ± 10 ms obtained from a single exponential fit (Figure 5b) is the same within error limits as the rise constant of ethane under identical H_2-N_2 flow conditions. This directly demonstrates that the ethane growth originates from hydrogenation of CH_3CH_2Pt species. Moreover, the rate within a factor of 2 of the TOF over a Pt(111) surface reported for steady state experiments (323 K, p_{C2H4} = 10 Torr, p_{H2} = 10 Torr, p_{N2} = 80 Torr).[31] As expected, the rate of surface ethyl decay increases with increasing H_2 flow, reflecting the dependence on H surface coverage. For example, the rates are 4.1 s^{-1} for H_2/N_2 = 0.027, and 8.2 s^{-1} for H_2/N_2 = 0.053.

In agreement with the known spectator role of ethylidyne, there is only a very small band observed at 1339 cm^{-1} immediately after the ethylene pulse (Figure 6a). The species grows in with a rise time of 150 ms, as shown in Figure 6b. The finding confirms the well-known fact that the rate of formation of CH_3CPt_3 is orders of magnitude lower than that of surface ethyl species.[1b]

3.2 Temperature Dependence of Surface Ethyl-to-Ethane Kinetics

At 473 K, the ethane growth was found to reach a maximum in the first time slice after the pulse.[26] The most striking observations upon decrease of the reaction temperature are the gradual appearance of an ethane growth on the tens to hundreds of ms scale, and a decrease of the prompt ethane component in the first time slice. The prompt C_2H_6 growth as fraction of the asymptotic growth decreases from 0.75 at 473 K to 0.44 at 323 K, as can be seen from Figure 7. Over the same temperature range from 473-323 K, the amount of surface ethyl (1200 cm^{-1}) observed in the initial t = 24 ms time slice increases 5-fold from A(1200 cm^{-1}) = 0.003 at 473 K to A(1200 cm^{-1}) = 0.014 at 323 K. By contrast, the temperature dependence of the first-order rate constant of the CH_3CH_2Pt decay is rather weak, decreasing form 6.9 s^{-1} at 473 to 4.1 s^{-1} at 323 K (H_2/N_2 = 0.027).

4. Discussion

Our observation by time-resolved FT-IR that the rise of ethane mirrors the decay time of CH_3CH_2Pt establishes the direct kinetic evidence for the surface ethyl as the kinetically relevant intermediate. This is to our knowledge the first direct proof of the kinetic significance of an observed intermediate in a heterogeneous catalytic reaction. Our finding that surface CH_3CH_2Pt is the rate-limiting species rather than π-C_2H_4 is supported by recent DFT calculations on ethylene hydrogenation over noble metals. The computations consistently predict the activation barrier of π-ethylene to ethyl hydrogenation (step 1) to be substantially lower than the ethyl hydrogenation barrier (step 2). DFT results for Pt by Miura *et al.* give $E_{a,1}$ of 4 kcal mol^{-1}, which is much smaller than $E_{a,2}$ of 27 kcal mol^{-1}.[24] A similar computational result was obtained by Neurock *et al.* for C_2H_4 hydrogenation over Pd surfaces, with $E_{a,1} = 9$ kcal mol^{-1} compared to $E_{a,2} = 17$ kcal mol^{-1}.[23] We conclude that surface ethyl to ethane interconversion is the rate determining step of ethylene hydrogenation under reaction conditions. The fact that the CH_3CH_2Pt growth is complete in a few ms at all temperatures examined (323-473 K) is in agreement with the low activation energy of step 1 predicted by the DFT calculations.

Prompt growth of ethane is observed at all temperatures. As can be seen from Figure 3b, at 323 K the single exponential fit of the absorbance growth of the 2893 cm^{-1} band predicts a substantial C_2H_6 yield at t = 0, about 10 percent of the asymptotic growth at that temperature. Clearly, part of the surface ethyl species react with substantially faster rates than the majority of the CH_3CH_2Pt intermediates. The most likely origin of the

dispersion of the first order rate constants is heterogeneity of the surface environment in which the reaction takes place, resulting in varying strength of interaction of the ethyl moiety with the Pt surface. The most weakly interacting intermediates are expected to exhibit the highest hydrogenation rates, the most strongly interacting ones the slowest rates. A recent computational study of C_2H_4 hydrogenation on Pd(111) by Neurock and Van Santen revealed a strong dependence of the C_2H_5-Pd bond strength on surface coverage.[23] Specifically, if the adsorbed ethyl and an adsorbed H share a Pd center, the intermediate is destabilized by 7 kcal mol^{-1} due to repulsive interaction, reducing the barrier of hydrogenation step 2 from 24 to 17 kcal mol^{-1}.[23] A likely origin for the dispersion of the ethyl to ethane hydrogenation rates on Pt/Al$_2$O$_3$ catalyst is therefore heterogeneity in the H distribution on the metal surface resulting in varying degree of destabilization of the C_2H_5Pt species. The fraction of ethyl intermediates undergoing hydrogenation prior to the 24 ms time slice is expected to increase with rising temperature at the expense of the amount of CH$_3$CH$_2$Pt formed, in agreement with the results of our measurements. On the other hand, the observed temperature dependence of the rate constant in the range 473–323 K is weak. This is to be expected for a limited measurement window (t > 24 ms) in the case of dispersive kinetics: as the temperature is lowered, ethyl species that are hydrogenated at t < 24 ms at the higher temperature become observable on the t > 24 ms scale, thereby masking the rate decrease of the slower (more stable) ethyl species.

The very large temperature dependence of the intensity ratio of the 2 surface species CH$_3$CH$_2$Pt and CH$_3$CPt$_3$ is worth noting. At 473 K, the 1200 cm^{-1} peak of ethyl and the

1339 cm^{-1} band of ethylidyne have the same intensity within a factor of 2, and both species exhibit the maximum buildup in the first spectrum after the pulse. By contrast, at 323 K, only the ethyl growth is complete at t < 24 ms while the ethylidyne band shows a factor of 10 lower intensity in the first time slice, and grows slowly on the hundreds of ms scale. The very large decrease of the rate of formation of ethylidyne from 473 to 323 K is consistent with the high barrier estimated for ethylene to ethylidyne dehydrogenation,[32] and confirms the orders of magnitude slower hydrogenation rate of CH_3CPt_3 compared to π-C_2H_4 and CH_3CH_2Pt.[1b] The explanation for the observation of similar amounts of ethyl and ethylidyne observed in the 473 K experiment is that most surface CH_3CH_2Pt are consumed by hydrogenation to C_2H_6 before the 24 ms spectrum is recorded. This results in only small amounts of ethyl species left unreacted on the tens of ms time scale.

5. Conclusions

FT-IR monitoring of ethylene hydrogenation over Pt/Al_2O_3 with a time resolution of 25 ms in the temperature range 323 to 473 K reveals surface ethyl as the rate-limiting reaction intermediate. The hydrogenation of ethylene to CH_3CH_2Pt is instantaneous on the ms time scale at all temperatures examined, indicating a substantially lower barrier compared to surface ethyl to ethane conversion. These observations are in agreement with recent DFT calculations reported in the literature. The decay of CH_3CH_2Pt was found to exhibit the same temporal behavior as the rise of C_2H_6, demonstrating directly

the kinetic significance of the surface ethyl intermediates for the first time. Dispersive

kinetics of the ethyl to ethane hydrogenation manifests the varying strength of interaction

of CH_3CH_2 with the Pt surface, which we attribute to heterogeneity of the surface

coverage. Computational work on ethylene hydrogenation over a Pd surface by Neurock

et al. suggests that the distribution of H on the metal surface is the likely cause of the

variation of the ethyl-surface interaction strength. At 323 K, the rise of the ethylidyne

spectator species is on the order of 200 ms, consistent with the much higher barrier of

ethylene dehydrogenation compared to hydrogenation at high surface coverage. As

expected, the rate of CH_3CPt_3 formation increases beyond the ms resolution limit of our

current experiment when raising the temperature to 473 K. While 25 millisecond time

resolution using the rapid-scan technique coupled with pulsed release of reactants

through a mechanical valve proved sufficient for the monitoring of ethyl to ethane

hydrogenation, the microsecond and nanosecond resolution of the step-scan FT-IR

technique will be required for monitoring the initial, ethylene to ethyl hydrogenation

step.[28]

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Figure Captions

Figure 1:   Rapid-scan survey spectra of $C_2H_4 + H_2$ reaction induced by ethylene

pulses over Pt/Al_2O_3 at 323 K recorded at 25 ms resolution. Times refer to

the time delay between the opening of the pulsed valve and the midpoint

of the corresponding interferogram slice. Spectra above 1600 cm^{-1} were

recorded with the 8 micron bandgap HgCdTe detector, those in the 1600-

800 cm^{-1} region with the 12 micron bandgap HgCdTe detector. The

derivative-type signal at 1250 cm^{-1} is an effect of the detector.

Figure 2:   Decrease of ethylene absorption (peak intensity of the 1890 cm^{-1} band)

caused by gas flow. A 3 micromol C_2H_4 pulse of 30 ms duration (85 psi

back pressure) was released into a continuous H_2-N_2 flow (4.5 L min^{-1}, 1

atm, $H_2/N_2 = 0.053$) at 323 K

Figure 3:   Rapid-scan spectra in the 3200-2700 cm^{-1} region observed following the

initiation of $C_2H_4 + H_2$ catalysis at 323 K. The ethylene bands have been

subtracted. The bottom trace shows the static spectrum of an authentic

ethane sample recorded with the same spectral parameters used for the

time-resolved $C_2H_4 + H_2$ runs. (b) Kinetics of ethane growth (peak

absorbance at 2893 cm^{-1}). The data points are corrected for absorbance

loss due to removal of ethane by gas flow (see text). The solid line

represents a single exponential fit.

Figure 4:   C-H stretch absorptions of surface ethyl and ethane at 24 and 107 ms after

              initiation of catalysis.

Figure 5:   Rapid-scan spectra in the 1250-1120 cm^{-1} region observed following the

              initiation of C_2H_4 + H_2 catalysis at 323 K. The solid curve of panel (b)

              represents a single exponential fit to the peak absorbance of the 1200 cm^{-1}

              CH_3CH_2Pt band.

Figure 6:   Rapid-scan spectra in the 1375-1275 cm^{-1} region observed following the

              initiation of C_2H_4 + H_2 catalysis at 323 K. A: t = 36 ms; B: t = 164 ms; C: t

              = 321 ms; D: t = 577 ms.

Figure 7:   Prompt growth of ethane upon C_2H_4 hydrogenation as function of

              temperature. The ratio corresponds to the ethane absorbance of the first

              time slice (24 ms) relative to the asymptotic C_2H_6 growth (2893 cm^{-1}).

              Data shown used a flow of 9 L min^{-1} and a H_2/N_2 ratio of 0.027.
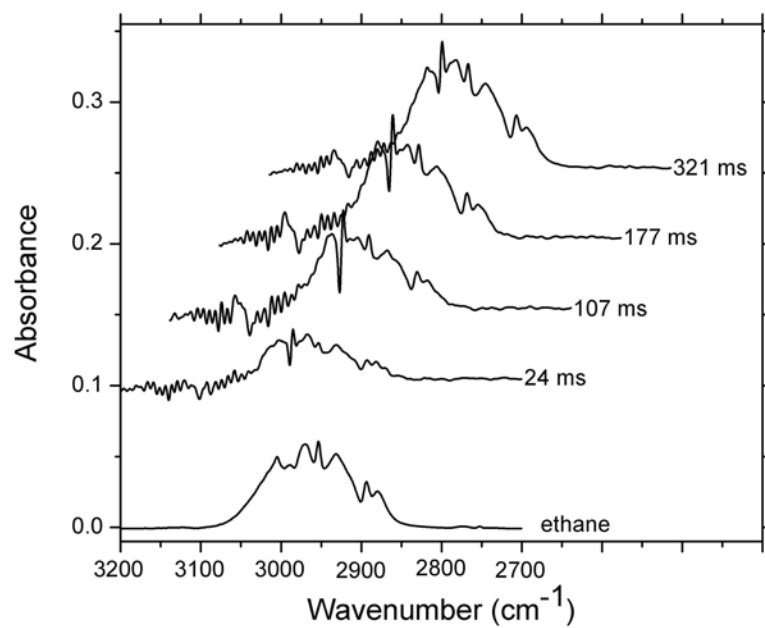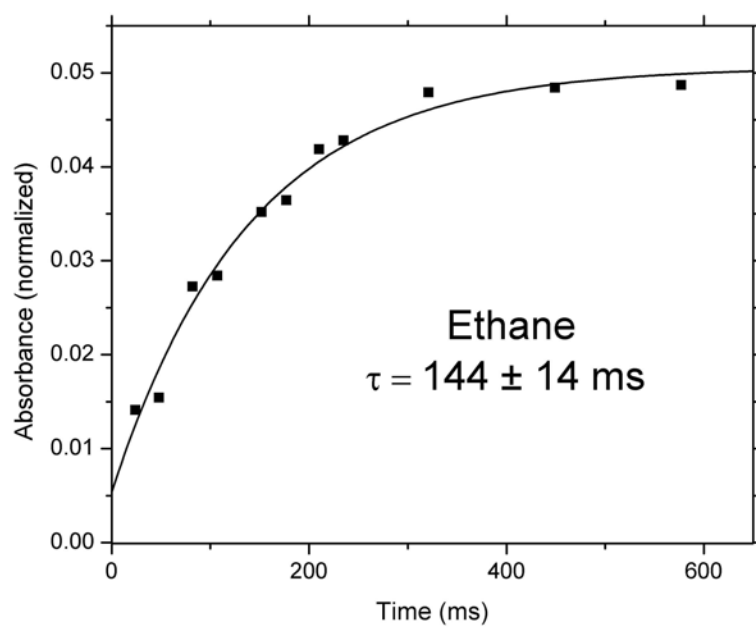
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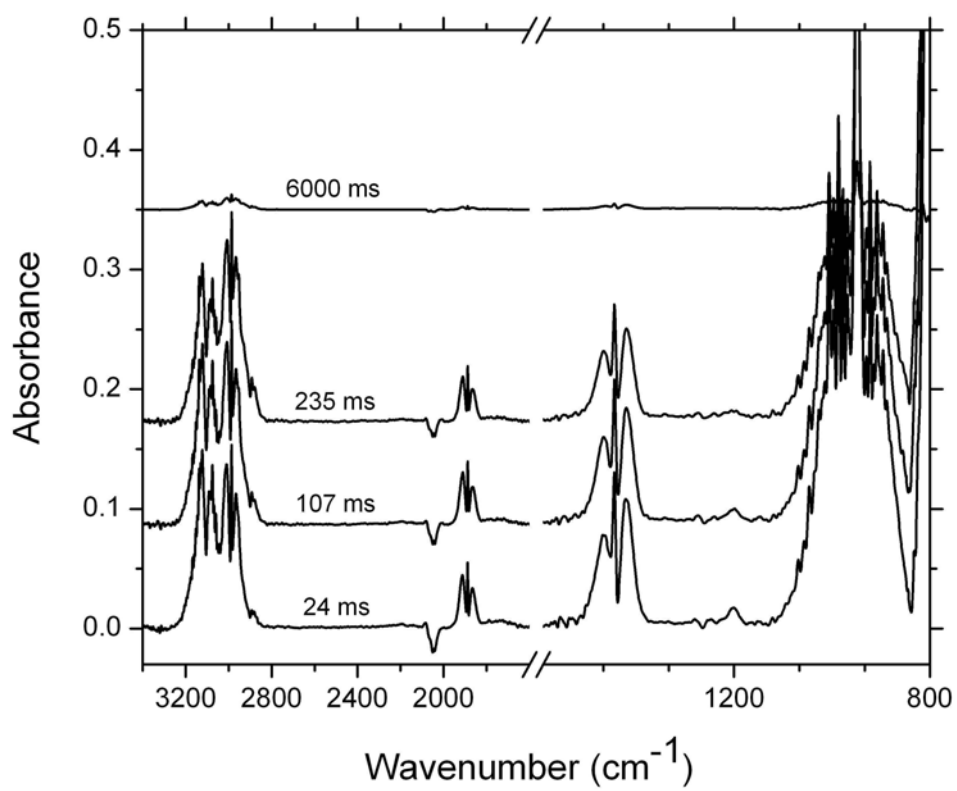
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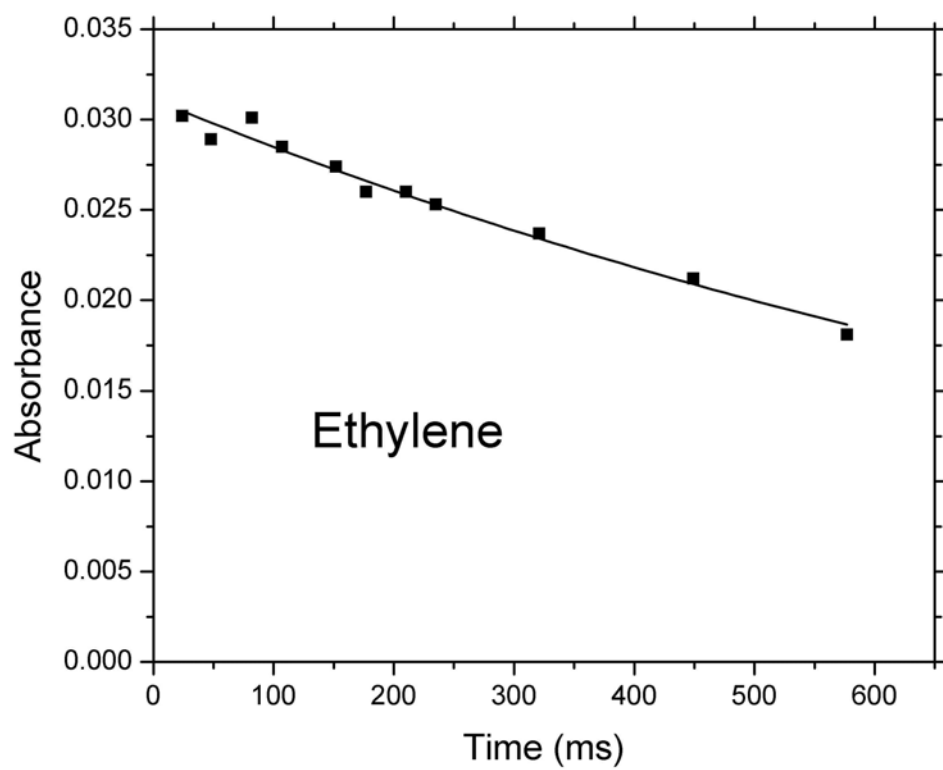
Figure 3a

Figure 3b

Figure 4
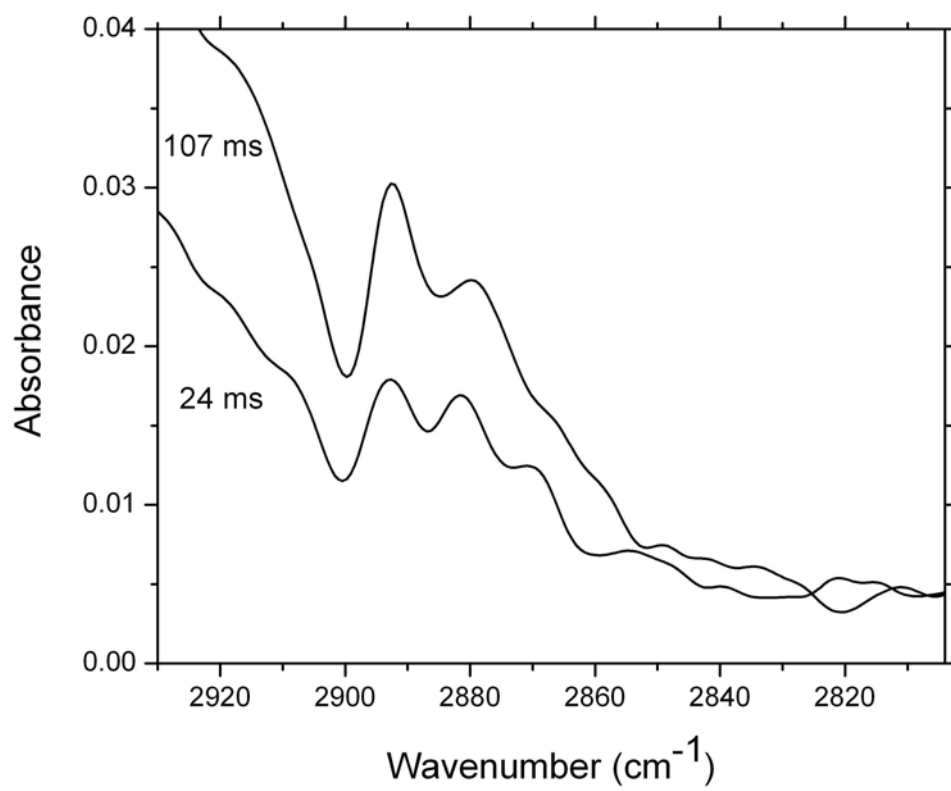
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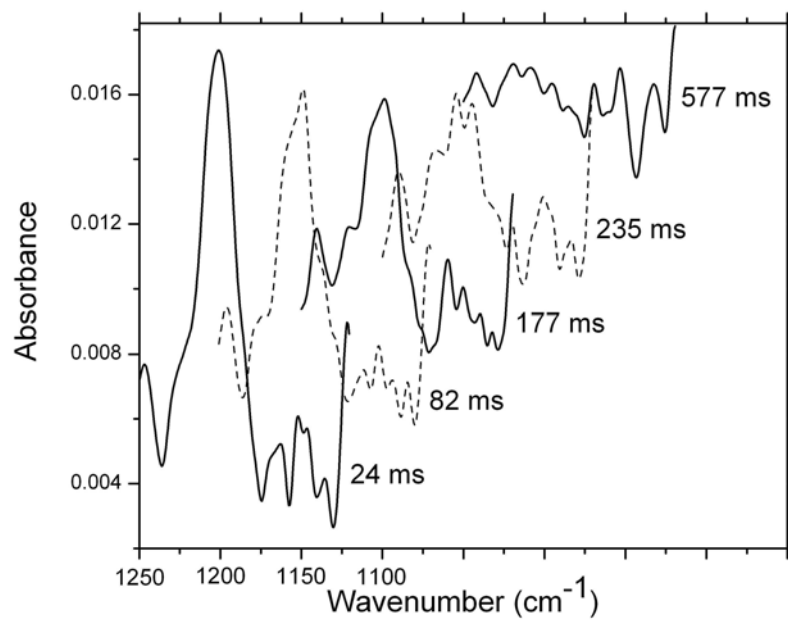
Figure 5b

Figure 6

Figure 7